FUEL ADDITIVES FOR FUEL CELL
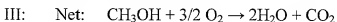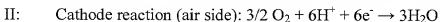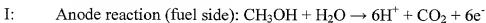
1 **Technical Field**

2   The technical field generally relates to fuel cells and in particular to fuel additives

3 that enhance performance of liquid-type fuel cells.

4 **Background**

5   A fuel cell is an electrochemical apparatus wherein chemical energy generated

6 from a combination of a fuel with an oxidant is converted to electric energy in the

7 presence of a catalyst. The fuel is fed to an anode, which has a negative polarity, and the

8 oxidant is fed to a cathode, which, conversely, has a positive polarity. The two electrodes

9 are connected within the fuel cell by an electrolyte to transmit protons from the anode to

10 the cathode. The electrolyte can be an acidic or an alkaline solution, or a solid polymer

11 ion-exchange membrane characterized by a high ionic conductivity. The solid polymer

12 electrolyte is often referred to as a proton exchange membrane (PEM).

13   In fuel cells employing liquid fuel, such as methanol, and an oxygen-containing

14 oxidant, such as air or pure oxygen, the methanol is oxidized at an anode catalyst layer to

15 produce protons and carbon dioxide. The protons migrate through the PEM from the

16 anode to the cathode. At a cathode catalyst layer, oxygen reacts with the protons to form

17 water. The anode and cathode reactions in this type of direct methanol fuel cell are

18 shown in the following equations:

19 I: Anode reaction (fuel side): $CH_3OH + H_2O \rightarrow 6H^+ + CO_2 + 6e^-$

20 II: Cathode reaction (air side): $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

21 III: Net: $CH_3OH + 3/2\ O_2 \rightarrow 2H_2O + CO_2$

22   The goal in methanol fuel processing is complete methanol oxidation for

23 maximum energy generation shown in the equation. Catalysts that promote the rates of

24 electrochemical reactions, such as oxygen reduction and hydrogen oxidation in a fuel cell

25 are often referred to as electrocatalysts. Electrocatalysts are important because the

26 energy efficiency of any fuel cell is determined, in part, by the overpotentials necessary at

27 the fuel cell's anode and cathode. In the absence of an electrocatalyst, a typical electrode

28 reaction occurs, if at all, only at very high overpotentials. Thus, the oxidation and

29 reduction reactions require catalysts in order to proceed at useful rates.

30 *Carbon monoxide (CO) poisoning of the catalyst*

31   Platinum (Pt), an expensive metal, is the best catalyst for many electrochemical

32 reactions, including methanol oxidation. A major obstacle in the development of

1 methanol fuel cells is the loss of electrochemical activity of even the best electrocatalyst

2 due to "poisoning" by CO. CO is an intermediate in the oxidation of methanol to carbon

3 dioxide (CO_2). CO is adsorbed at the surface of the Pt due to its special molecular

4 structure and thus blocks the access of new fuel molecules to the catalytically active Pt

5 centers.

6   CO is a severe poison to Pt electrocatalysts. It significantly reduces fuel cell

7 performance even at levels of 1-10 ppm. A fuel cell which would be useful for

8 commercial applications would preferably be tolerant of CO levels produced in a

9 relatively uncomplicated fuel system, i.e., 100 ppm or greater.

10   Substantial effort has been devoted to developing a multi-element catalyst such as

11 Pt-Ru and Pt-Ru-Os. The addition of Ruthenium (Ru), for example, helps convert CO

12 into CO_2 and relieves the Pt from being poisoned. Attempts have also been made to

13 further reduce the CO concentration, and particularly through a selective oxidation

14 process for the CO. Conventionally, the oxidation of CO to CO_2 occurs in the presence of

15 a catalyst and at temperatures above 150°C.

16   PEM fuel cells, which have potential application in mass transportation, are very

17 sensitive to CO poisoning. Conventional PEM membranes, such as NAFION^{TM}, must

18 contain significant amounts of water to conduct protons from the electrode reactions.

19 Accordingly, PEM fuel cells cannot operate at temperatures over about 100°C, and

20 preferably operate at temperatures around 80°C. At these operating temperatures, CO

21 strongly adsorbs to the Pt catalyst to poison the fuel cell performance.

22   Thus, there remains a need to reduce the level of CO in the fuel system to improve

23 liquid-type fuel cell performance in an effective and commercially viable manner.

24 *Wettability of the electrodes*

25   Adequate wetting of the electrodes is another major problem for liquid-type fuel

26 cells. To provide a large reaction area, the electrode structures in a liquid-type fuel cell

27 need to be very porous and the liquid fuel solution needs to wet all pores. In addition,

28 CO_2 that is evolved at the fuel side electrode needs to be effectively released from the

29 zone of reaction. Adequate wetting enhances the release of CO_2 from the electrode. In

30 PEM fuel cells, the PEM also requires water to be effective in conducting protons.

31   Conventional gas diffusion type fuel cell anode structures are not suitable for use

32 in liquid-type fuel cells. These conventional electrodes have poor fuel wetting properties.

33 The conventional electrodes, however, can be modified for use in liquid-type fuel cells by

1   coating them with an electrode additive that improve their wetting properties, such as

2   NAFION^{TM} which also serves as a PEM.

3   US Pat. No. 6,248,460 describes a method of wetting an electrode within a liquid-

4   type fuel cell having a sulfuric acid electrolyte by employing perfluorooctanesulfonic acid

5   as an additive to the fuel mixture of the fuel cell. However, the invention is directed to a

6   very specific application, i.e., improving performance of fuel cells having a sulfuric acid

7   electrolyte, and is not applicable to other types of liquid-type fuel cells, such as fuel cells

8   having a PEM.

9   *"Futile oxidation" at the anode*

10   As shown in equation II, the cathode of liquid-type fuel cells is exposed to air

11   where the protons react with oxygen to produce water. Some oxygen will inevitably

12   dissolve in the fuel and will be carried to the anode side of the fuel cell. The oxygen will

13   then be oxidized into oxygen ions by the catalyst on the anode. The oxygen ions will then

14   react with the protons produced on the anode by equation I, and form water on the anode.

15   This "futile oxidation" prevents the transfer of protons from the anode to the cathode and

16   hence diminishes the current generated by the fuel cell reaction. There remains a need to

17   efficiently remove the dissolved oxygen from the fuel of a liquid type fuel cell.

18   *Impurities in the fuel*

19   Impurities in the fuel of a fuel cell may inhibit the desired electrochemical

20   reaction. For example: a methanol based liquid fuel may contain trace amount of sulphur

21   or metal ions, such as Fe^{++}, Cu^{++}, Cr^{+}, Ni^{+}, and Zn^{++}, that are detrimental to the electrolyte

22   and/or catalyst. The impurities may originate from the fuel supply itself or enter the fuel

23   from elsewhere in the system. Some of the impurities may be chemically adsorbed or

24   physically deposited on the surface of the anode catalyst, blocking the active catalyst sites

25   and preventing these portions of the anode catalyst from inducing the desired

26   electrochemical fuel oxidation reaction.

27   In the absence of countermeasures, the adsorption or deposition of catalyst

28   poisons may be cumulative, so even minute concentrations of poisons in a fuel stream,

29   may, over time, result in a degree of catalyst poisoning which is detrimental to fuel cell

30   performance.

31   Conventional methods for addressing the problem of fuel impurities include

32   physical filtration and/or chemical treatment of the fuel to remove the impurities. The

33   purification process can be tedious and expensive, and requires specially designed

34   equipment.

1   **Summary**

2   A method of enhancing performance of liquid-type fuel cells by adding additives

3   to the liquid fuel is disclosed. Different additives may be employed to perform different

4   functions, such as reducing CO poisoning of the catalyst, increasing wettability of the

5   electrodes, or removing dissolved oxygen and impurities in the fuel. The additives may

6   be used individually, or premixed in a desired ratio for a given type of fuel cell. The

7   additives may be used on a regular basis to improve fuel efficiency and prolong the life

8   span of fuel cells. The additives may also be pre-packed for field use when high quality

9   fuel is not available. These additives thus provide a convenient and cost-effective way of

10   improving performance of a liquid-type fuel cell.

11   In an embodiment, hemoglobin may be used as an additive to absorb CO in the

12   fuel and prevent CO poisoning of the catalyst in a fuel cell.

13   In another embodiment, a wettability control agent, such as a surfactant, may be

14   used as an additive to improve the wetting of the porous electrode.

15   In another embodiment, an oxygen scavenger, such as ascorbate, may be used as

16   an additive to remove oxygen dissolved in the fuel and prevent the futile oxidation on the

17   anode of the fuel cell.

18   In yet another embodiment, a chelating agent, such as EDTA, may be used as an

19   additive to remove metal ions from the fuel to prevent the poisoning of the electrode.

20   Additional advantages and novel features will be set forth in part in the

21   description which follows, and in part will become apparent to those skilled in the art

22   upon examination of the following or may be learned by practice of the invention.

23   **Detailed Description**

24   A variety of materials can be used as fuel additives for fuel cell applications.

25   Different materials may serve different functions. In an embodiment, hemoglobin may be

26   used as a fuel additive to prevent CO poisoning of Pt based catalyst.

27   Hemoglobin is the major component of red blood cells which transport oxygen

28   from the lungs to body tissues and facilitates the return transport of CO_2. Hemoglobin is

29   a 64,400 kD protein. Each hemoglobin molecule is a tetramer of four smaller polypeptide

30   subunits known as globins. A hemo group, which is an iron-protoporphyrin complex, is

31   associated with each polypeptide subunit, and is responsible for the reversible binding of

32   a single molecule of oxygen. Normal adult hemoglobin is made up of two different kinds

33   of polypeptide globins. A first globin, known as alpha globin, contains 141 amino acid

34   residues. The second, known as beta globin, contains 146 amino acid residues. In normal

1   adult hemoglobin, two of each kind of globin are arranged in the form of a truncated

2   tetrahedron which has the overall shape of an ellipsoid.

3   Ligands that bind hemoglobin include CO, NO, CN^-, and the most physiologically

4   relevant ligand, oxygen. CO is well known to be highly toxic to the oxygen transport

5   function of hemoglobin. In humans, a small amount of CO will cause serious problems, a

6   blood CO concentration of 400 ppm will result in headache and discomfort, and 4000

7   ppm can be fatal in less than one hour. The reason for this toxicity is that hemoglobin is

8   235 times more reactive to CO than to oxygen. Binding of CO molecules to hemoglobin

9   decreases the total oxygen carrying capacity of blood by rendering a portion of the

10   hemoglobin molecule unusable for oxygen binding, it also shifts the conformation of the

11   remaining hemoglobin molecule such that the hemoglobin binds the oxygen more avidly,

12   thus making it more difficult for oxygen to be released to the tissues and therefore

13   starving the tissue and organs of vital oxygen supplies. In other words, CO binds to

14   hemoglobin in a way similar to its binding to Pt. Therefore, hemoglobin may be used as a

15   fuel additive to preferentially bind CO and relieve the Pt catalyst from being poisoned by

16   CO.

17   Hemoglobin is available in either powder or liquid form. The powder form can be

18   dissolved in water or water containing fuels. It is available from, for example, Sigma-

19   Aldrich Inc. The liquid form is available from Biopure as Oxyglobin® solution.

20   Generally, the amount of hemoglobin that may be added to the fuel is in the range

21   of 0.0001-1% by weight.

22   In another embodiment, the additive may be a surfactant that decreases interfacial

23   tension of the liquid/catalyst interface and leads to the uniform wetting of the electrode

24   pores and particles by the fuel and water solution, yielding enhanced utilization of the

25   electrocatalyst. Further, the improved wettability also facilitates the release of carbon

26   dioxide from the pores of the electrode.

27   The surfactant may be an anionic, cationic, amphoteric, nonionic surfactant, or a

28   mixture of compatible surfactants.

29   Examples of anionic surfactants are water-soluble soaps or water-soluble synthetic

30   surface active compounds. Examples of the soaps are unsubstituted or substituted

31   ammonium salts of higher fatty acids (C10 -C22), such as the sodium or potassium salts

32   of oleic acid or stearic acid or of natural fatty acid mixtures such as coconut oil or tallow

33   oil, alkali metal salts, alkaline earth metal salts or fatty acid methyllaurin salts. Examples

1   of synthetic surfactants are alkylarylsulphonates, sulphonated benzimidazole derivatives,
2   fatty alcohol sulphates, or fatty alcohol sulphonates.

3   Examples of alkylarylsulphonates are the calcium, sodium or triethanolamine salts
4   of dodecylbenzenesulphonic acid, dibutylnaphthalenesulphonic acid, of a condensate of
5   naphthalenesulphonic acid and formaldehyde or the phosphate salt of the phosphoric acid
6   ester of an adduct of p-nonylphenol with 4 to 14 moles of ethylene oxide. Examples of
7   sulphonated benzimidazole derivatives are 2 sulphonic acid groups and one fatty acid
8   radical containing approximately 8 to 22 carbon atoms. Examples of fatty alcohol
9   sulphates or sulphonates are unsubstituted or substituted ammonium salts such as C8 -
10 C22 alkyl radical including the alkyl moiety of acyl radicals such as the calcium or
11 sodium salt of lignosulphonic acid, of a mixture of fatty alcohol sulphates from naturally
12 occurring fatty acids, of dodecylsulphate, alkali metal salts or alkaline earth metal salts or
13 the salts of sulphated and sulphonated fatty alcohol/ethylene oxide adducts.

14   Examples of non-ionic surfactants are polyglycol ether derivatives of aliphatic or
15 cycloaliphatic alcohols having approximately 3 to 30 glycol ether groups and
16 approximtely 8 to 20 carbon atoms in the (aliphatic) hydrocarbon moiety; saturated or
17 unsaturated fatty acid and alkylphenols having approximately 6 to 18 carbon atoms in the
18 alkyl moiety of the alkylphenols; water-soluble adducts of polyethylene oxide with
19 ethylenediaminopolypropylene glycol, polypropylene glycol, or alkylpolypropylene
20 glycol having approximately 1 to 10 carbon atoms in the alkyl chain, having
21 approximately 20 to 250 ethylene glycol ether groups and approximately 10 to 100
22 propylene glycol ether groups in the usual ratio of 1 to 5 ethylene glycol
23 moiety:propylene glycol moiety; fatty acid esters of polyoxyethylene sorbitan such as
24 polyoxyethylene sorbitan trioleate; octylphenoxypolyethoxyethanol; polyethylene glycol;
25 tributylphenoxypolyethyleneethanol; polypropylene/polyethlene oxide adducts; castor oil
26 polyplycol ethers; nonylphenolpolyethoxyethanols.

27   Examples of cationic surfactants are quaternary ammonium salts in the form of
28 halides, methylsulphates or ethylsulphates which have as N-substituent at least one C8 -
29 C22 alkyl radical or unsubstituted or halogenated lower alkyl or benzyl or hydroxy-lower
30 alkyl radicals, such as stearyltrimethylammonium chloride or benzyldi(2-
31 chloroethyl)ethylammonium bromide.

32   Examples of amphoteric surfactants are the aminocarboxylic and aminosulphonic
33 acids and salts thereof such as alkali metal 3-(dodecylamino)propionate and alkali metal

1   3-(dodecylamino)propane-1-sulphonate or alkyl and alkylamido betaines such as

2   cocamidopropyl betaine.

3   Examples of surfactants which may be used in the combination are surfactants from the

4   Teric.RTM. series such as N4 Teric, Teric BL8, Teric 16A16, Teric PE61, Alkanate

5   3SL3, N9 Teric, G9 A6 Teric or from the Rhodafac.RTM series such as Rhodafac RA

6   600. Further examples are Calgon.RTM (sodium hexametaphosphate), Borax.RTM

7   (sodium decahydrate borate), soap, sodium lauryl sulphate, or sodium cholate.

8   Generally, the amount of surfactant that may be added to the liquid fuel is in the

9   range of 0.0001-1% by weight.

10   In another embodiment, the fuel additive may be an oxygen scavenger that

11   absorbs oxygen in the fuel and therefore, reduces the futile oxidative reaction on the

12   anode. Examples of oxygen scavengers include, but are not limited to, sodium sulfite,

13   sodium bisulfite, ascorbate, hydrazine, hydroquinone, benzmay, and sulfhydryl

14   compounds.

15   Generally, the amount of oxygen scavenger that may be added to the liquid fuel is

16   in the range of 0.0001- 1% by weight.

17   In yet another embodiment, the fuel additive may be a chelating agent that

18   removes the metal ions that have a detrimental effect on the electrodes. Examples of

19   chelating agents include, but are not limited to, ethylenediaminetetraacetic acid (EDTA)

20   and trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA), and salts thereof.

21   Generally, the amount of chelating agent that may be added to the liquid fuel is in

22   the range of 0.0001- 1% by weight.

23   The additives may be added individually based on needs, or pre-mixed in a

24   desired ratio for a given type of fuel cell. The additives can be used on a regular basis to

25   improve fuel efficiency and prolong the life span of fuel cells. They can also be pre-

26   packed for field use when high quality fuel is not available. These additives thus provide

27   a convenient and cost-effective way of improving performance of liquid type fuel cells.

28   Although preferred embodiments and their advantages have been described in

29   detail, various changes, substitutions and alterations can be made herein without

30   departing from the spirit and scope of the fuel additives as defined by the appended

31   claims and their equivalents.